

## CLAIMS

### WHAT IS CLAIMED IS:

1. A method for solid free-form fabrication of a three-dimensional object, comprising:
  - depositing a particulate blend in a defined region, said particulate blend including a calcium phosphate source, a reaction retardant, and a layered double hydroxide; and
  - selectively ink-jetting a solubilizing binder onto a predetermined volume of said particulate blend to form a pre-ceramic object in said predetermined volume, wherein said solubilizing binder includes wetting agents, humectants, acidic or basic pH modifiers, and surfactants.
2. The method of claim 1, further comprising removing a portion of said particulate blend that does not form said pre-ceramic object.
3. The method of claim 1, wherein said forming a pre-ceramic object further comprises performing a re-precipitation setting reaction.
4. The method of claim 3, wherein said re-precipitation setting reaction produces a hydroxyapatite.
5. The method of claim 1, further comprising firing said pre-ceramic object to form a ceramic object.
6. The method of claim 5, wherein said firing comprises:
  - drying said pre-ceramic object; and
  - sintering said pre-ceramic object to form a ceramic.
7. The method of claim 5, further comprising performing a finishing operation on said ceramic object.

8. The method of claim 7, wherein said finishing operation comprises one of a grinding operation, a lapping operation, an ultrasonic machining operation, a chemical machining operation, an electrical-discharge machining operation, or a glazing operation.

9. The method of claim 1, wherein said calcium phosphate source comprises one of a tetracalcium phosphate, a monocalcium phosphate (MCP), a monocalcium phosphate monohydrate (MCPM), a  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , a dicalcium phosphate (DCP), a dicalcium phosphate dihydrate (DCPD), a  $\text{CaHPO}_4$ , a  $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ , an  $\alpha$ -tricalcium phosphate, a  $\beta$ -tricalcium phosphate, or hydroxyapatite.

10. The method of claim 1, wherein said particulate blend further comprises a reaction accelerant.

11. The method of claim 10, wherein said reaction accelerant comprises one of a lithium phosphate, an aluminum nitrate, or an iron nitrate.

12. The method of claim 11, wherein said particulate blend further comprises polyacids.

13. The method of claim 12, wherein said polyacids comprise one of a polyvinyl phosphoric acid, a homo- or a copolymer of unsaturated aliphatic carbonic acid, a polyvinyl sulphonic acid, a polystyrene sulphonic acid, or a polyacrylic acid (PAA).

14. The method of claim 1, wherein said reaction retardant comprises one of a citric acid, an oxalic acid, an ethylenediamine tetraacetic acid, a sodium phosphate, a tartaric acid, or a salicylic acid.

15. The method of claim 1, wherein said layered double hydroxide comprises one of CaAl-LDH, MgAl-LDH, ZnAl-LDH, CaAl-LDH, MgAl-LDH, or ZnAl-LDH .

16. The method of claim 15, wherein said layered double hydroxide comprises a phosphate, a sulfate, a nitrate, a carbonate, or a polyanion, wherein said phosphate, sulfate, nitrate, carbonate, or polyanion is intercalated into said layered double hydroxide.

17. The method of claim 15, wherein said layered double hydroxide is based on one of magnesium, zinc, aluminum, calcium, or iron.

18. The method of claim 1, wherein said particulate blend comprises:  
tetracalcium phosphate;  
citric acid;  
CaAl-LDH (NO<sub>3</sub>);  
poly acrylic acid (60k);  
Li<sub>3</sub>PO<sub>4</sub>; and  
magnesium fluoride.

19. The method of claim 1, wherein said solubilizing binder comprises:  
phosphoric acid (H<sub>3</sub>PO<sub>4</sub>);  
2-pyrrolidone;  
liponic ethylene glycol (LEG-1);  
SURFYNOL 465;  
Water;  
1,5-pentanediol; and  
TERGITOL-15-s-7.

20. The method of claim 19, wherein said solubilizing binder comprises an acidic pH of 2.5.

21. The method of claim 1, wherein said acidic pH modifiers comprise one of a phosphoric acid ( $H_3PO_4$ ), a mineral acid, a phytic acid, an acetic acid, or an ethanoic acid.

22. The method of claim 1, wherein said basic pH modifiers comprise one of a potassium hydroxide (KOH), a lithium hydroxide (LiOH), a sodium hydroxide (NaOH), a NH<sub>4</sub>OH, an aluminum hydroxide (Al(OH)<sub>3</sub>), a magnesium hydroxide (Mg(OH)<sub>2</sub>), a calcium hydroxide (Ca(OH)<sub>2</sub>), or a barium hydroxide (Ba(OH)<sub>2</sub>).

23. The method of claim 1, wherein said pre-ceramic object comprises a shell defining the outer surface of said three-dimensional object.

24. The method of claim 1, wherein said solubilizing binder further comprises a colorant.

25. A system for solid free-form fabrication of a three-dimensional object comprising:

a particulate blend including a calcium phosphate source, a reaction retardant, and a layered double hydroxide; and

a solubilizing binder configured to hydrate said particulate blend to form a pre-ceramic object.

26. The system of claim 25, wherein said solubilizing binder comprises a wetting agent, a humectant, pH modifiers, and a surfactant.

27. The system of claim 26, wherein said pre-ceramic object is configured to be fired to form a ceramic object.

28. The system of claim 27, wherein said ceramic object has a compression modulus of over 14 Giga-Pascals.

29. The system of claim 25, wherein said calcium phosphate source comprises one of a tetracalcium phosphate, a monocalcium phosphate (MCP), a monocalcium phosphate monohydrate (MCPM), a  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , a dicalcium phosphate (DCP), a dicalcium phosphate dehydrate (DCPD), a  $\text{CaHPO}_4$ , a  $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ , an  $\alpha$ -tricalcium phosphate, a  $\beta$ -tricalcium phosphate or hydroxyapatite.

30. The system of claim 25, wherein said particulate blend further comprises a reaction accelerant.

31. The system of claim 30, wherein said reaction accelerant comprises one of a lithium phosphate, an aluminum nitrate, or an iron nitrate.

32. The system of claim 31, wherein said particulate blend further comprises polyacids.

33. The system of claim 32, wherein said polyacids comprise one of a polyvinyl phosphoric acid, a homo- or a copolymer of unsaturated aliphatic carbonic acid, a polyvinyl sulphonic acid, a polystyrene sulphonic acid, or a polyacrylic acid (PAA).

34. The system of claim 25, wherein said reaction retardant comprises one of a citric acid, an oxalic acid, an ethylenediamine tetraacetic acid, a sodium phosphate, a tartaric acid, or a salicylic acid.

35. The system of claim 25, wherein said layered double hydroxide comprises one of CaAl-LDH, MgAl-LDH, ZnAl-LDH, CaAl-LDH, MgAl-LDH or ZnAl-LDH.

36. The system of claim 35, wherein said layered double hydroxide comprises a phosphate, a sulfate, a nitrate, a carbonate, or a polyanion,

wherein said phosphate, sulfate, nitrate, carbonate, or polyanion is intercalated into said layered double hydroxide.

37. The system of claim 35, wherein said layered double hydroxide is based on one of magnesium, zinc, aluminum, calcium, or iron.

38. The system of claim 25, wherein said particulate blend comprises:  
tetracalcium phosphate;  
citric acid;  
CaAl-LDH (NO<sub>3</sub>);  
polyacrylic acid (60k);  
Li<sub>3</sub>PO<sub>4</sub>; and  
magnesium fluoride.

39. The system of claim 25, wherein said solubilizing binder comprises:

phosphoric acid (H<sub>3</sub>PO<sub>4</sub>);  
2-pyrrolidone;  
liponic ethylene glycol (LEG-1);  
SURFYNOL 465;  
Water;  
1,5-pentanediol; and  
TERGITOL-15-s-7.

40. The system of claim 39, wherein said solubilizing binder comprises an acidic pH of 2.5.

41. The method of claim 26, wherein said pH modifiers comprise one of a phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), a mineral acid, a phytic acid, an acetic acid, or an ethanoic acid.

42. The method of claim 26, wherein said pH modifiers comprise one of a potassium hydroxide (KOH), a lithium hydroxide (LiOH), a sodium hydroxide (NaOH), a NH<sub>4</sub>OH, an aluminum hydroxide (Al(OH)<sub>3</sub>), a magnesium hydroxide (Mg(OH)<sub>2</sub>), a calcium hydroxide (Ca(OH)<sub>2</sub>), or a barium hydroxide (Ba(OH)<sub>2</sub>).

43. The system of claim 25, wherein said pre-ceramic object comprises hydroxyapatite formed by a dissolution and a subsequent reprecipitation of a calcium phosphate.

44. The system of claim 25, further comprising an ink-jet material dispenser configured to selectively jet said solubilizing binder onto said particulate blend.

45. The system of claim 44, wherein said ink-jet material dispenser comprises one of a thermally actuated inkjet dispenser, a mechanically actuated inkjet dispenser, an electrostatically actuated inkjet dispenser, a magnetically actuated inkjet dispenser, a piezoelectrically actuated inkjet dispenser, or a continuous inkjet dispenser.

46. The system of claim 44, further comprising a substrate configured to support said particulate blend in a defined region, said defined region being configured with respect to said ink-jet material dispenser such that said solubilizing binder, upon being jetted from said ink-jet material dispenser, selectively contacts said particulate blend.

47. The system of claim 44, wherein said system is configured to apply a pre-determined volume of binder of said solubilizing binder.

48. The system of claim 25, further comprising a furnace configured to provide thermal energy to said pre-ceramic object sufficient to sinter said pre-ceramic object.

49. A solid three-dimensional prototype composition, comprising:  
multiple layers of pre-ceramic deposited in contact with one another,  
each of said multiple layers of pre-ceramic comprising a particulate blend  
including a calcium phosphate source, a reaction retardant, and a layered  
double hydroxide;  
wherein said particulate blend was hydrated by a solubilizing binder to  
produce said pre-ceramic.

50. The composition of claim 49, wherein said pre-ceramic comprises  
hydroxyapatite.

51. The composition of claim 49, wherein said ink-jettable aqueous  
binder comprises:  
wetting agents;  
humectants; and  
surfactants.

52. The composition of claim 49, wherein said particulate blend  
comprises:  
tetracalcium phosphate;  
citric acid;  
CaAl-LDH (NO<sub>3</sub>);  
poly acrylic acid (60k);  
Li<sub>3</sub>PO<sub>4</sub>; and  
magnesium fluoride.

53. The composition of claim 49, wherein said pre-ceramic has a  
compression modulus of 0.05 Giga-Pascal.

54. The composition of claim 49, wherein said pre-ceramic is  
configured to produce a ceramic upon firing.

55. The composition of claim 54, wherein said ceramic is configured to have a compression modulus over 14.0 Giga-Pascal.

56. A system for solid free-form fabrication of a three-dimensional object comprising:

a particulate blend including a calcium phosphate source, a reaction retardant, and a layered double hydroxide; and

a means for solubilizing said particulate blend to form a pre-ceramic object.

57. The system of claim 56, wherein said pre-ceramic object comprises hydroxyapatite.

58. The system of claim 57, wherein said hydroxyapatite is formed by a dissolution and a subsequent reprecipitation of calcium phosphate.

59. The system of claim 58, further comprising a means for selectively dispensing said means for solubilizing onto said particulate blend.

60. The system of claim 59, wherein said dispensing means comprises one of a thermally actuated inkjet dispenser, a mechanically actuated inkjet dispenser, an electrostatically actuated inkjet dispenser, a magnetically actuated inkjet dispenser, a piezoelectrically actuated inkjet dispenser, or a continuous inkjet dispenser.

61. The system of claim 58, further comprising means for supporting said particulate blend in a defined region, said defined region being configured with respect to said selective dispensing means such that said solubilizing means, upon being jettied from said selective dispensing means, contacts said particulate blend.

62. The system of claim 56, further comprising a means for heating said pre-ceramic object, wherein said heating means is configured to provide sufficient thermal energy to said pre-ceramic object to sinter said pre-ceramic object.